



Short communication

Reactions of metallic Li or LiC₆ with organic solvents for lithium ion battery

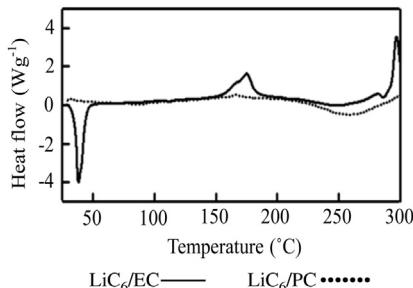
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HIGHLIGHTS

- EC more easily reacts with metallic Li and LiC₆ than PC.
- EC more easily forms lithium alkyl carbonate than PC.
- DEC, EMC and DMC react with Li in the same manner.

GRAPHICAL ABSTRACT



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ABSTRACT

DSC (Differential Scanning Calorimetry) study has been made on the reactions of metallic Li or LiC₆ with organic solvents for lithium ion battery. Ethylene carbonate (EC) more easily reacts with metallic Li and LiC₆ than propylene carbonate (PC). This may be because formation of lithium alkyl carbonate is more difficult for PC than EC. On the other hand, diethyl carbonate (DEC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) react with Li in the same manner. Reactions of Li and LiC₆ with organic solvents have been discussed based on the results of quantum calculation.

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1. Introduction

Since lithium ion battery uses flammable organic solvents, there is a possibility of firing or explosion of the battery at high temperatures, by short circuit formation, by overcharging and so on. High safety is required to avoid these accidents especially for the application to the electric sources of hybrid cars and electric vehicles. Thermal stability of lithium ion battery is therefore an

important research subject. In our group, the effect of organo-fluorine compounds on the thermal stability and electrochemical properties of graphite has been investigated in ethylene carbonate (EC)-based and propylene carbonate (PC)-mixed electrolyte solutions [1–5]. It has been found that mixing of fluorine compounds effectively improves thermal and oxidation stability of electrolyte solutions. This would be attributed to the low reactivity of with Li and high oxidation stability of fluorine compounds [5]. It was already reported that EC, dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) react with Li, yielding lithium alkyl carbonates such as (CH₂OCO₂Li)₂ and ROCO₂Li (R: CH₃, C₂H₅) [6–11]. Reduction mechanisms of these solvents were also

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reported [9–11]. Li-intercalated graphite, LiC_6 starts to decompose above ca. 100 °C [7]. Therefore exothermic peaks due to the reactions of LiC_6 with organic solvents and solid electrolyte interphase (SEI) are observed above 130 °C in DSC (Differential Scanning Calorimetry) study [3–5,7]. Thermal decomposition of electrolyte solutions and SEI takes place at higher temperatures than ca. 200 °C [3–5,7,12–18]. This means that the reactivity of Li with organic solvents is important because it occurs at lower temperatures than those for thermal decomposition of electrolyte solutions and SEI. In this paper, the reactivity of metallic Li and LiC_6 with organic solvents is reported.

2. Experimental

DSC measurement was carried out using a mixture of metallic Li or LiC_6 and EC, PC, DEC, EMC or DMC between room temperature and 300 °C at a temperature increasing rate of 5 °C min^{−1} (DSC-60, Shimadzu). Sample mixtures were sealed in aluminum cell for DSC in a glove box. Lithiated graphite samples were electrochemically prepared in 1 mol L^{−1} LiPF_6 –EC/DMC (1:1 vol.) after 2 cycles. Host graphite was natural graphite powder (purity: >99.95%) with average particle size of 10 µm (NG10 µm). The d_{002} value obtained by X-ray diffractometry (XRD-6100, Shimadzu) was 0.3354 nm. Surface area and meso-pore volume obtained by BET surface area measurement (Tristar 3000, Shimadzu) were 9.2 m² g^{−1} and 0.035 cm³ g^{−1}, respectively. D-band to G-band intensity ($R = I_D/I_G$) obtained by Raman spectroscopy (NRS-1000, Jasco) with Nd:YVO₄ laser (532 nm) was 0.23. Composition of Li-intercalated graphite samples was calculated from discharge capacity to be $\text{Li}_{0.85–0.99}\text{C}_6$. Lithiated graphite samples used for DSC measurements were 1.4–1.6 mg. Electrolyte solution and metallic Li were 3 µL and 9–11 mg, respectively. In the case of EC, 4 mg of solid EC was sealed in aluminum cell with metallic Li or LiC_6 . To discuss about the reactions of Li with organic solvents, bond lengths and electrostatic charges of oxygen and carbon of organic solvent molecules were calculated by semi-empirical AM1 method using Spartan '06.

3. Results and discussion

Fig. 1 shows DSC profiles for a mixture of metallic Li and EC or PC. Endothermic peaks were observed at 38 and 182 °C, indicating the melting of EC and metallic Li, respectively. No exothermic reaction was observed below 182 °C probably because metallic Li was covered by thin oxide film which prevented the reactions of Li with EC and PC. As soon as metallic Li melted, reaction of Li with EC started, giving an exothermic peak at 217 °C. On the other hand, PC is more stable than EC against Li. The reaction of Li with PC started at 234 °C and its peak position was situated at 257 °C. Fig. 2 shows DSC curves for mixtures of metallic Li and DEC, EMC or DMC. Strong

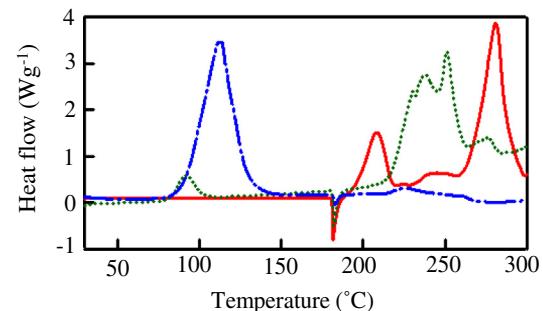


Fig. 2. DSC curves for mixtures of metallic Li and DEC, EMC or DMC. Li/DEC —●—, Li/EMC —●—, Li/DMC —●—.

exothermic peak for Li/DEC mixture started to increase at 80 °C. This would be due to the reaction of Li with DEC, being different from another reaction such as decomposition of Li/DEC complex, which would be an endothermic reaction like the dissociation of LiPF_6 to LiF and PF_5 . Weak exothermic peak for Li/EMC mixture also started at 80 °C. Exothermic peaks were located at 112 °C and 92 °C below the melting point of Li for DEC and EMC, respectively, while several peaks were found above 180 °C for DMC. This may be attributed to the lower surface tensions of DEC, EMC and DMC than those of EC and PC (DEC: 24.5, (40 °C) and 18.0 mN m^{−1} (100 °C) [19], DMC: 26.3 (39 °C) and 17.8 mN m^{−1} (100 °C) [20], EC: 42.2 mN m^{−1} (40 °C), PC: 39.6 mN m^{−1} (40 °C)). Additionally the boiling points of DEC, EMC and DMC are 127, 107 and 90 °C, respectively [21]. Therefore DMC and most of EMC vaporize before reacting with Li. However, DEC having the higher boiling point is able to permeate through the crack of surface oxide film of Li due to its lower surface tension, giving an exothermic peak at 112 °C by the reaction with Li. Some exothermic peaks by the reaction with Li and thermal decomposition were observed between 200 and 300 °C for EMC and DMC.

Reactions of LiC_6 with organic solvents gave different DSC profiles as shown in Figs. 3 and 4. Li-intercalated graphite, LiC_6 decomposes above 100 °C, releasing fresh Li [7]. Fig. 3 indicates that EC reacted with Li deintercalated from graphite, giving an exothermic peak at 174 °C while PC did not exhibit an exothermic peak up to 300 °C. On the other hand, DEC, EMC and DMC showed the similar DSC curves to each other, providing exothermic peaks due to the reactions with deintercalated Li at 130–135 °C. Exothermic peaks above 250 °C may be due to thermal decomposition of organic solvents and SEI.

Lithium alkyl dicarbonate, $(\text{CH}_2\text{OCO}_2\text{Li})_2$ is experimentally confirmed main product by the reaction of EC with LiC_6 [6–11]. The formation of $(\text{CH}_2\text{OCO}_2\text{Li})_2$ may consist of two step reactions. The

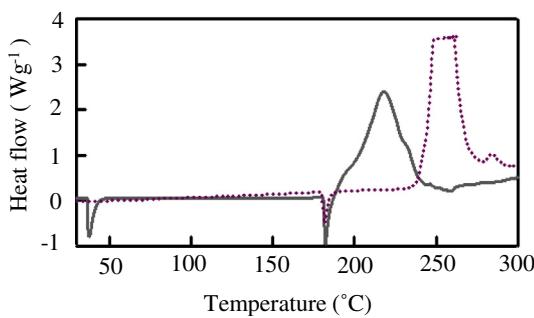


Fig. 1. DSC curves for mixtures of metallic Li and EC or PC. Li/EC —●—, Li/PC —●—.

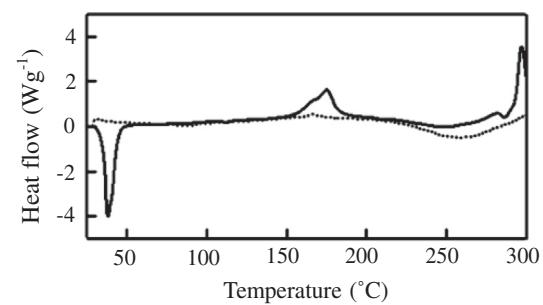


Fig. 3. DSC curves for $\text{Li}_{0.99}\text{C}_6/\text{EC}$ and $\text{Li}_{0.96}\text{C}_6/\text{PC}$ mixtures. $\text{Li}_{0.99}\text{C}_6/\text{EC}$ —●—, $\text{Li}_{0.96}\text{C}_6/\text{PC}$ —●—.

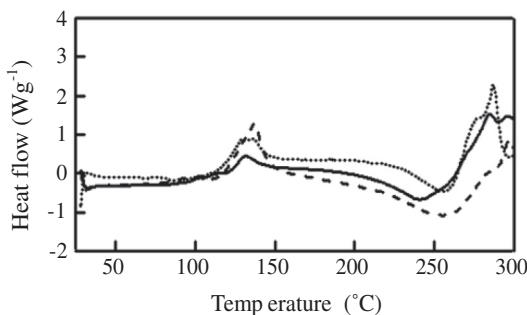
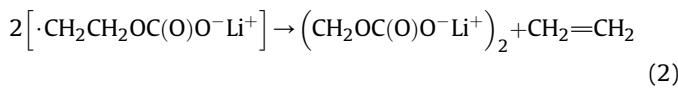
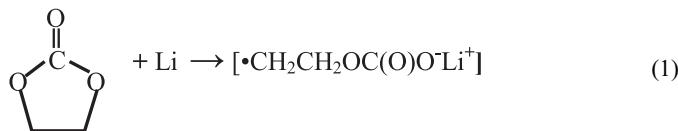
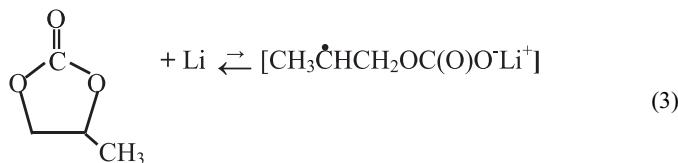


Fig. 4. DSC curves for $\text{Li}_{0.97}\text{C}_6/\text{DEC}$, $\text{Li}_{0.95}\text{C}_6/\text{EMC}$ and $\text{Li}_{0.85}\text{C}_6/\text{DMC}$ mixtures. $\text{Li}_{0.97}\text{C}_6/\text{DEC}$ —, $\text{Li}_{0.95}\text{C}_6/\text{EMC}$ - - -, $\text{Li}_{0.85}\text{C}_6/\text{DMC}$

first one may be a radical formation reaction (1) and second one a kind of dimerization reaction of two radical species.



The results of DSC measurements shown in Figs. 1 and 3 suggest that lithium alkyl dicarbonate, $(\text{CH}_2\text{OC(O)O}^-\text{Li}^+)_2$ is smoothly formed. On the contrary, the reaction of PC with Li or LiC_6 does not proceed well as shown in Figs. 1 and 3, respectively. According to the result of calculation given in Table 1, the $\text{C}-\text{O}$ bond is slightly longer, that is, more ionic in $-\text{O}-\text{CH}(\text{CH}_3)-$ group (1.451 nm) than $-\text{O}-\text{CH}_2-$ group (1.441 nm) in PC, which coincides with that the electrostatic charge of oxygen atom is lower in $-\text{O}-\text{CH}(\text{CH}_3)-$ group (E: -0.445) than $-\text{O}-\text{CH}_2-$ group (E: -0.411), and that of carbon atom bonded to oxygen is higher in $-\text{O}-\text{CH}(\text{CH}_3)-$ group (E: +0.200) than in $-\text{O}-\text{CH}_2-$ group (E: -0.096). This suggests that $\text{C}-\text{O}$ bond in $-\text{O}-\text{CH}(\text{CH}_3)-$ group is more easily broken than that in $-\text{O}-\text{CH}_2-$ group by the reaction with Li to form a radical as given in Equation (3). However, a combination of two radicals such as dimerization reaction similar to Equation (2) may be difficult to occur due to the presence of a methyl group. It means that the reaction of PC with



Li does not smoothly proceed. This may be the reason why PC is more stable than EC against Li and LiC₆. PC did not react with Li

Table 1
Bond lengths and electrostatic charges of oxygen and carbon of PC.

<u>C</u> – <u>Q</u> bond	<u>Q</u> = <u>C</u> <	– <u>Q</u> – <u>CH</u> ₂ –	– <u>Q</u> – <u>CH</u> (<u>CH</u> ₃)–
C–Q bond length (nm)	1.216	1.441	1.451
Electrostatic charge of Q	–0.504	–0.411	–0.445
Electrostatic charge of C	0.908	–0.096	+0.200

Table 2
Bond lengths and electrostatic charges of oxygen and carbon of EC.

<u>C–O</u> bond	<u>O=C<</u>	<u>–O–CH₂–</u>
<u>C–O</u> bond length (nm)	1.215	1.442
Electrostatic charge of <u>O</u>	–0.514	–0.414
Electrostatic charge of <u>C</u>	0.939	–0.066

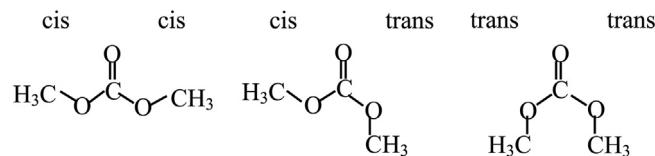
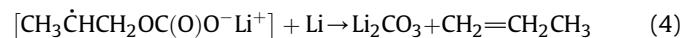


Fig. 5. Possible conformations of DMC.

when $\text{Li}_{0.96}\text{C}_6$ was used (Fig. 3), but reacted with Li at the higher temperature than the reaction temperature of EC when metallic Li was used because the amount of metallic Li was much larger than that of Li deintercalated from graphite (Figs. 1 and 3). The radical species formed in Equation (3) may further react with Li if enough amount of Li exists. A possible reaction is the formation of Li_2CO_3 as given in Equation (4) as previously reported [11]. The difficulty in the formation of lithium alkyl carbonate may be the main reason why PC is electrochemically decomposed on graphite without formation of SEI.



On the other hand, $\text{C}-\text{O}$ bond length of $-\text{O}-\text{CH}_2-$ group in EC is 1.442 nm and electrostatic charges of carbon and oxygen atoms in $-\text{O}-\text{CH}_2-$ group are -0.066 and -0.414, respectively (Table 2). The $\text{C}-\text{O}$ bond length of $-\text{O}-\text{CH}_2-$ group in EC (1.442 nm) is shorter than that of $-\text{O}-\text{CH}(\text{CH}_3)-$ group in PC (1.451 nm), being close to that of $-\text{O}-\text{CH}_2-$ group of PC (1.441 nm) as given in Tables 1 and 2. This may be consistent with that electrochemical reduction of PC starts at slightly higher potential than that for EC and continues between 1.0 and 1.6 V [9,11].

Linear carbonates, DEC, EMC and DMC can take several different conformations, that is, the $-\text{CH}_3$ and/or $-\text{C}_2\text{H}_5$ ligand can take *cis* or *trans* conformation with respect to $\text{O}=\text{C}(-\text{O}-)_2$. Possible conformations of DMC are shown in Fig. 5 as examples. In the case of linear carbonates, lithium alkyl carbonates can be formed by one step reactions as given in Equations (5)–(7). This would make easier the reactions of DEC, EMC and DMC with Li than those of PC and EC.

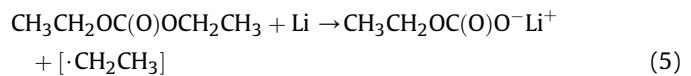


Table 3
Bond lengths and electrostatic charges of oxygen and carbon of DEC.

Conformation	cis-cis		cis		trans
C–O bond	$O=C<$	–O–CH ₂ CH ₃	$O=C<$	–O–CH ₂ CH ₃	–O–CH ₂ CH ₃
C–O bond length (nm)	1.230	1.448	1.226	1.445	1.445
Electrostatic charge of O	–0.634	–0.454	–0.579	–0.461	–0.435
Electrostatic charge of C	0.967	0.119	0.933	0.082	0.121

Table 4

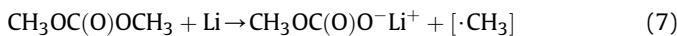
Bond lengths and electrostatic charges of oxygen and carbon of EMC.

Conformation	cis	cis	cis	trans	trans	trans	cis
C–O bond	O=C<	–O–CH ₃	–O–CH ₂ CH ₃	O=C<	–O–CH ₃	–O–CH ₂ CH ₃	O=C<
C–O bond length (nm)	1.230	1.435	1.448	1.226	1.433	1.446	1.226
Electrostatic charge of O	−0.619	−0.414	−0.472	−0.569	−0.430	−0.452	−0.581
Electrostatic charge of C	0.987	−0.172	0.119	0.962	−0.216	0.109	0.930
							−0.171
							0.052

Table 5

Bond lengths and electrostatic charges of oxygen and carbon of DMC.

Conformation	cis–cis	cis	trans	trans–trans
C–O bond	O=C<	–O–CH ₃	O=C<	–O–CH ₃
C–O bond length (nm)	1.229	1.435	1.225	1.433
Electrostatic charge of O	−0.606	−0.432	−0.570	−0.395
Electrostatic charge of C	0.997	−0.147	0.957	−0.234
				−0.164
				0.940
				−0.146



Therefore their exothermic peaks would have been observed at 130–135 °C lower than 174 °C for EC (Figs. 3 and 4). C–O bond lengths and electrostatic charges of oxygen and carbon are slightly different depending on their conformations as given in Tables 3–5. The C–O bond lengths in $-\text{O}-\text{CH}_3$ and $-\text{O}-\text{CH}_2\text{CH}_3$ are in the range of 1.428–1.435 and 1.445–1.448 nm, respectively (Tables 3–5), which are longer than the C–O bond lengths in carbonate group, $\text{O}=\text{C}(-\text{O}-)_2$ (DEC: 1.348–1.358, EMC: 1.347–1.360 and DMC: 1.349–1.361 nm). This suggests that the C–O bond of $-\text{O}-\text{CH}_3$ or $-\text{O}-\text{CH}_2\text{CH}_3$ is more easily broken by the reaction with Li or electrochemical reduction. In case of EMC, the C–O bond of $-\text{O}-\text{CH}_2\text{CH}_3$ group has higher possibility to be broken because the C–O bond is longer in $-\text{O}-\text{CH}_2\text{CH}_3$ than in $-\text{O}-\text{CH}_3$ as given in Table 4.

4. Conclusions

Reactions of metallic Li or LiC_6 with organic solvents have been studied by DSC. EC easily reacted with metallic Li just after melting of Li (182 °C) while PC gave an exothermic peak at 257 °C higher than 217 °C for EC. In the reactions with LiC_6 , EC showed an exothermic peak at 174 °C. However, PC did not react with LiC_6 up to 300 °C. This would be attributed to that EC smoothly yields lithium alkyl dicarbonate by the reaction with Li while PC has a difficulty in the formation of similar lithium alkyl carbonate. When PC reacts with metallic Li (not LiC_6), enough amount of Li exists. In such a case, a radical formed by the reaction of PC with Li may further react with Li, giving Li_2CO_3 . Linear carbonates, DEC, EMC and DMC reacted with LiC_6 in the same manner, giving exothermic peaks at 130–135 °C though the reactions with metallic Li showed different DSC profiles due to their lower surface tensions and boiling points than those for EC and PC. Linear carbonates gave their exothermic peaks at 130–135 °C lower than 174 °C for EC because they can easily yield lithium alkyl carbonates by one step reactions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2013.05.138>.

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